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A CALORIMETER DESIGNED TO DETERMINE THE HEAT-OF-REACTION OF β-HMX AS A FUNCTION OF PRESSURE

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A constant volume – "constant pressure" combustion calorimeter for measuring the heat generated by burning small samples of explosives at any fixed test pressure to 68,900 kPa (10,000 psi) is described. The heat-of-reaction measurement is determined within 345 kPa (50 psi) of the test pressure. The explosive β-HMX is shown to undergo a reaction transition between 20,700 and 34,500 kPa (3000 and 5000 psi) during which its heat-of-reaction (Q) increases 4.27×10^5 J/kg (102 ± 6 cal/g). This transition occurs in the same pressure region as

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20.   ABSTRACT (contd)

the discontinuity in burning rate previously observed for experimental gun
propellants containing this explosive.   The presence of this transition may
lead to an explanation of this phenomenon.

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INTRODUCTION

When β-HMX is incorporated in experimental gun propellants, abrupt changes in the burning rate vs pressure slope are noted. This discontinutity usually appears near 27,600 to 34,500 kPa (4000 to 5000 psi) and the magnitude of the transition increases with HMX particle size. This is a preliminary investigation to determine whether or not the HMX undergoes a corresponding reaction transition in this pressure range.

APPROACH

In standard calorimetry, large quantities of sample are burned in a relatively small volume to obtain reasonably accurate heat-of-reaction values. Samples of this size produce large pressure differentials within which reaction temperatures, reactions, and products can vary. The final heat output is consequently an average value where pressure activated changes in reaction chemistry cannot be observed.

A calorimeter was, therefore, designed in which very small samples are burned and vented to a large, pre-pressurized volume (700cc). A pressure rise on the order of 345 kPa (50 psi) is obtained which allows discrimination of the heat-of-reaction within this pressure throughout the pre-pressure ranges of the test. The calorimeter is sensitive enough to measure the small temperature rise produced by this small sample and any reaction transition that may occur as a function of pressure will be reflected by a change in the heat-of-reaction.

RESULTS AND DISCUSSION

A heat-of-reaction transition was observed for 92, 45, and 4.1 micron-size samples of β-HMX. This transition occurs between 20,700 and 34,500 kPa (3000 and 5000 psi). The heat-of-reaction increases 4.27 ± 0.26 x 10^5 J/kg (102 ± 6 cal/g) over this pressure range with no changes immediately before or after this transition up to a pressure of 68,900 kPa (10,000 psi) (fig. 1). The pressure vs heat-of-reaction curves generated for the three samples are virtually identical indicating that the 6.8% heat energy increase is independent of the HMX particle size. The individual values for the three sample sizes are listed in table 1.

The reaction transition, although activiated in the pressure range 20,700 to 34,500 kPA (3000 to 5000 psi), is actually controlled by the temperature of the reaction. The reaction temperature increases with pressure because as the pressure increases it confines the reaction zone closer to the surface of the reactants. This concentrates the zone of burning causing higher reaction temperatures with higher pressures.

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Table

Heat-of-reaction vs pressure, β-HMX

$J/kg \times 10^6$

Pressure kPa (psi)	4.1 Micron	45 Micron	92 Micron	Average
68,900 (10,000)	6.691 (1598)	----	----	
62,100 (9,000)	6.682 (1596)	----	----	
55,200 (8,000)	6.695 (1599)	6.695 (1599)	6.703 (1601)	
48,300 (7,000)	6.670 (1593)	6.691 (1598)	6.708 (1602)	
41,400 (6,000)	6.686 (1597)	6.686 (1597)	6.682 (1596)	
34,500 (5,000)	6.665 (1592)	6.674 (1594)	6.670 (1593)	6.686 ± 0.013 (1597 ± 3 cal/g)
27,600 (4,000)	6.594 (1575)	6.565 (1568)	6.695 (1599)	Transition
24,100 (3,500)	6.485 (1549)	6.439 (1538)	6.427 (1535)	Region
20,700 (3,000)	6.295 (1495)	6.277 (1497)	6.268 (1497)	
17,200 (2,500)	6.276 (1499)	6.263 (1496)	6.268 (1497)	
13,800 (2,000)	6.255 (1494)	6.268 (1497)	6.272 (1498)	
11,200 (1,625)	----	6.234 (1489)	----	

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Table (contd)

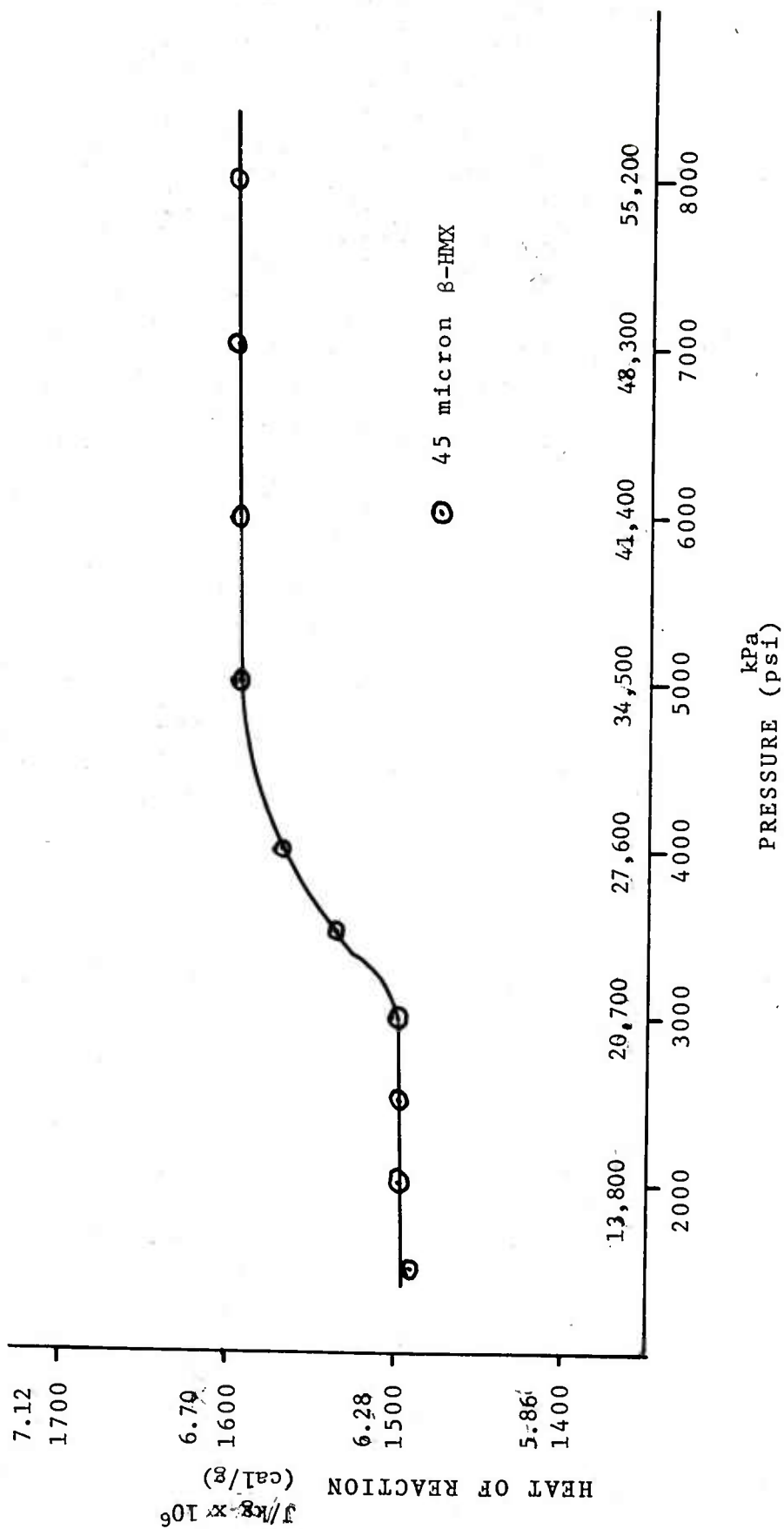| Pressure kPa (psi)	4.1 Micron	45 Micron	92 Micron	Average
10,300 (1,500)	6.247 (1492)	-----	6.230 (1488)	
8,600 (1,250)	-----	6.259 (1495)	-----	6.259 ± 0.013 (1495 ± 3 cal/g)
				4.27 ± 0.26 x 10^5 J/kg
			$\Delta Q =$	(102 ± 6)

Figure 1. Heat-of-reaction vs pressure profile.

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It is therefore reasonable to assume that the reaction transitions of β-HMX can occur at other pressures if alternate means are used to influence the reaction temperature.

APPARATUS AND PROCEDURE

The calorimeter is a low-heat-capacity, nickel-plated, copper, heat-exchange device which is mounted in a container which can be pressurized (a high pressure propellant strand burner). The body of the calorimeter (fig. 2) is open to the containing vessel and is at equilibrium with the pressurized N_2 environment. When a 50 mg sample of HMX is burned in the calorimeter, its combustion products must follow a tortuous route through nesting copper sleeves and a spiral pathway, during which the calorimeter extracts the heat energy. The temperature rises, and the calorimeter comes to equilibrium with the pre-pressurized environment.

The burning of the sample within the calorimeter is initially localized with a 0.25 mm thick-walled, stainless steel baffle. This aids in the uniform distribution of heat to the outer walls of the calorimeter by preventing hot-spot heat transfer.

The calorimeter (purged and pre-pressurized at some N_2 pressure) is operated isothermally, requiring initial and final heat-leak corrections. It was convenient to introduce the major heat-leak at the beginning of the run, where its path is quite predictable, at a rate that would produce a zero final heat-leak. The slope of the initial heat-leak was adjusted by introducing or releasing surges of N_2 gas until the desired heat-leak was obtained. The heat-leak corrections were applied to the 50% apportioning point by standard graphical techniques (fig. 3).

Complete combustion of the 50 mg sample was essential. To do this, a finely coiled one-mil platinum ignition wire was threaded in the center of a two-inch square pad of Dow Corning glass-wool filtering fibre. This pad was placed on a balance and 50 mg of β-HMX (weighed to ± 0.01 mg) were placed on the ignition coil. The pad was then carefully folded into a ball covering the coil and sample, and was closed by tying it with heat-treated glass sleeving. All extraneous material was trimmed and the protruding ignition wires fastened to the electrodes of the calorimeter. The HMX used was from the same batch of military grade HMX used to make the experimental propellants.

It appears that upon ignition the initial gases are able to pass freely through the porous, glass-wool while the HMX particles are localized for a sufficient period of time to complete its burning.
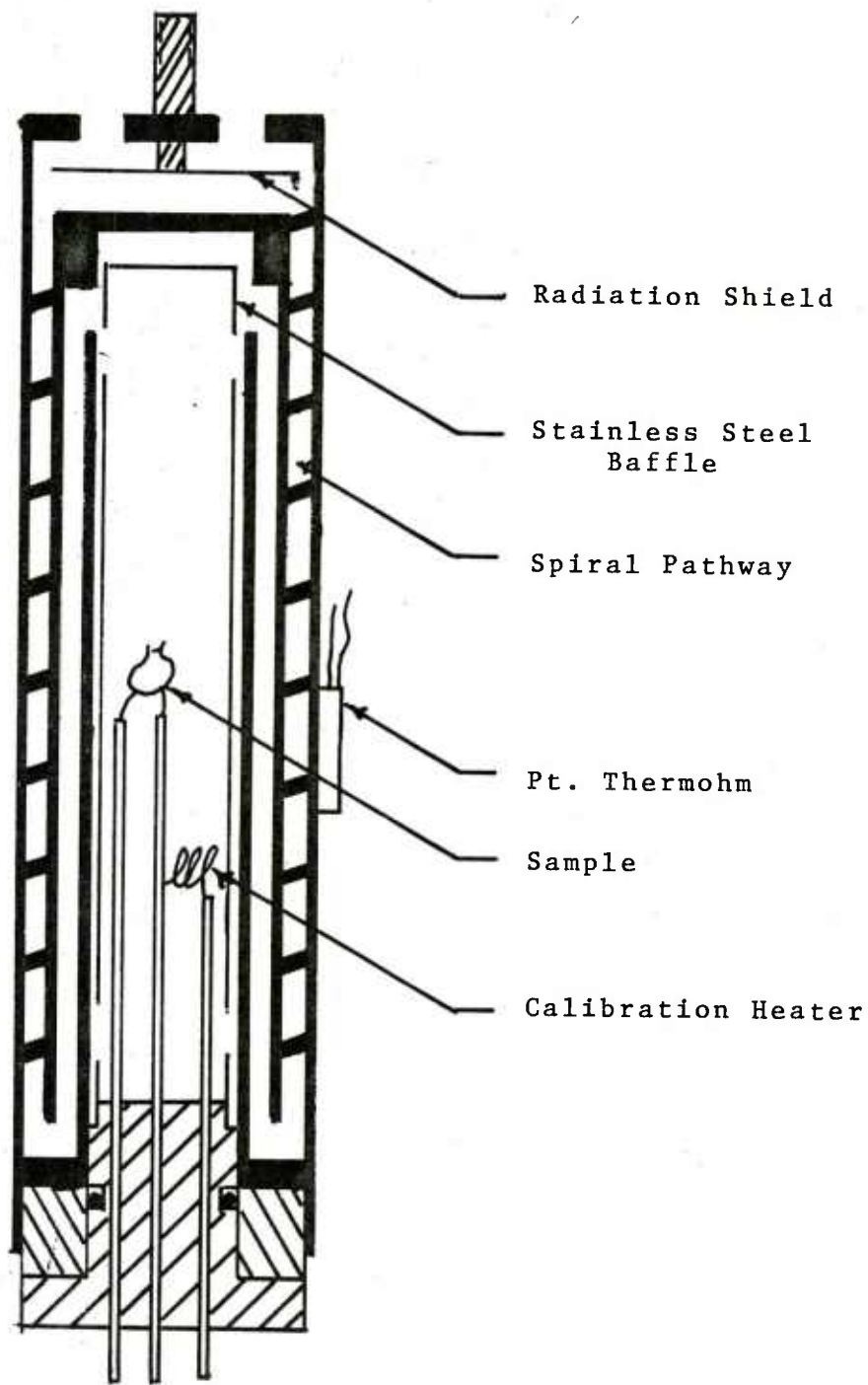
Figure 2. Constant volume – "constant pressure" calorimeter.
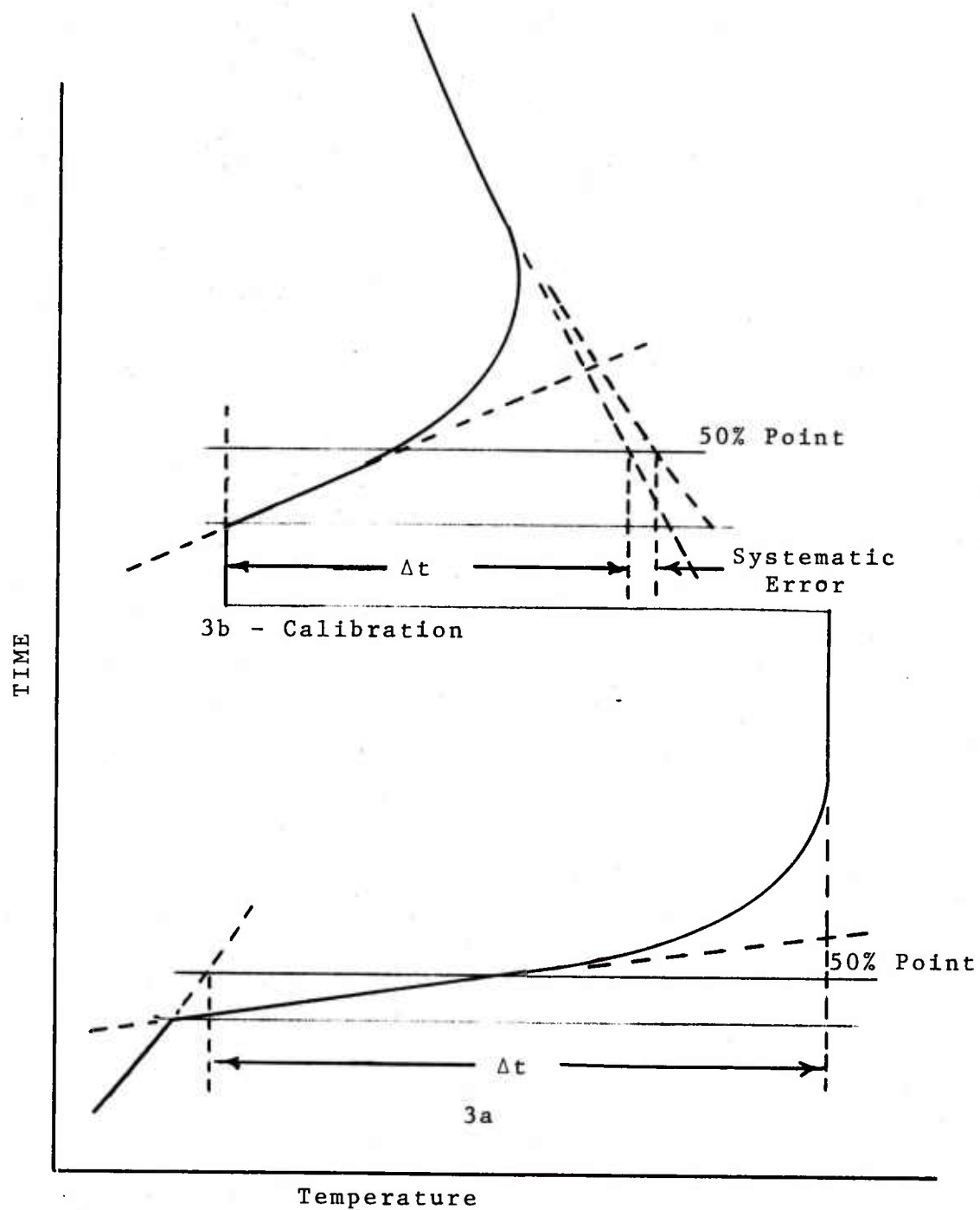
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Figure 3. Corrections for heat-leak.

The reproducibility of the data indicates that relatively complete combustion is obtained.

The heat capacity of the calorimeter depends upon the pressure at which the run is made in addition to its material and mass. Since the combination of pre-pressure and temperature is difficult to reproduce, electrical calibrations were made after each run with the combustion products and pressurized N_2 present.

Temperature Measurement

A 400-ohm, model 172A6C4X platinum resistance thermohm, manufactured by the Rosemount Engineering Co., was placed within a copper sleeve which was soldered to the outer wall of the calorimeter midway along its length (fig. 2). Thermal contact between the thermohm and the sleeve was aided with Dow Corning 340 Silicone Heat-Sink Compound.

The thermohm was operated at a monitored 0.9 ma. Its voltage drop was opposed with a current-balanced, bucking voltage. The resulting null signal was then amplified with a Kiethly model 149 amplifier and recorded on a Leeds & Northrup Speedomax XL strip chart recorder. Instrumentation settings were selected so that three-quarters of full-scale deflection (with associated heat-leaks) would be obtained for each measurement.

Calibration

A permanent, 30-ohm calibration heater was mounted within the calorimeter. This heater was made from Formex-coated, 29 gage, Evenohm resistance wire. It was threaded through Ben-Har heat-treated glass sleeving, compacted, and mounted within the calorimeter. Prior to use it was electrically heated to red heat until all volatiles were driven off. The voltage drop across the heater and the current through an appropriate standard resistor were measured with a Hewlett Packard Model 3460B digital voltmeter while the duration of the energy input was timed with a Hewlett Packard Model 522B digital timer.

The ignition energy was timed and measured for each run with a Tektronix model 5103N dual-beam oscilloscope. The ignition energy was on the order of 0.4 joules for each run.

Errors Due To Heat-Leak

The data listed in table 1 is determined with a precision of ± 0.2%. In terms of accuracy, however, it contains systematic errors which cause the reported values to be 100 cal/g higher than they should be. This, however, does not create a serious problem because the

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major interest is in obtaining a reproducible heat-of- reaction measurement with respect to pressure so that reaction transitions might be observed. An error in the absolute heat-of-reaction value can be tolerated as long as the error is constant.

The systematic error is introduced to circumvent an inherent weakness in the calorimeter which arises because it is operated isothermally and is mounted in a massive steel vessel to contain the high pre-pressurized environment. As the temperature changes in the calorimeter, thermal gradients are established in the containing vessel which can generate severe calorimetric heat-leaks. A problem arises because there is a bend in the curve representing these heat-leaks (fig 3) that can be difficult to extrapolate correctly to the 50% apportioning point. The major heat-leak errors are, therefore, concentrated in the final heat-leak of the calibration where the magnitude of the error can be kept reasonably constant.

This is done by selecting the slope of the initial heat-leak (fig. 3) through experience, so that the final calorimetric heat-leak is near zero. The path of this initial heat-leak is quite predictable and easily extrapolated to the apportioning point. The measurement of ΔT for the actual run is, therefore, reasonably accurate as well as precise. This degree of accuracy, however, is not maintained for the calibration that must follow (fig. 3b).

The calibration is performed electrically and, since the rate of energy input is slower than it is when HMX is burned, the calorimeter requires a longer time interval to attain equilibrium. This calibration starts with the zero heat-leak of the preceding run and generates a negative final heat-leak which, because of the slower rate of energy input, reaches equilibrium a significantly long distance from the apportioning point. This final heat-leak contains a gentle bend which is difficult to extrapolate correctly back to the apportioning point. It is, therefore, extrapolated back linearly from the range where equilibrium is obtained. This lodges the major errors caused by heat-leak in this correction and generates a calibration factor that is higher than it should be. To keep the magnitude of this error relatively constant, similar curves for each calibration were obtained by controlling the time and rate of energy input.

The heat-of-reaction values derived from this calibration factor for each run are, therefore, uniformly high. An indication of how high is obtained from the heat-of-reaction (Q) of β-HMX as determined by standard calorimetric procedures. In this procedure the HMX burns through a pressure gradient of 2,590 to 13,800 kPa (375 to 2000 psi) which corresponds to the pre-transition region of this work. The heat-of-reaction value is 5.832×10^6 J/kg (1393 ± 6 cal/g) as compared to

6.259 x 10^6 J/kg (1495 ± 3 cal/g) obtained in the constant volume-"constant pressure" calorimeter. It is assumed that the lower value is correct and that the introduced systematic error in the value reported is, therefore, on the order of 4.195 x 10^5 J/kg (100 cal/g). Since this error appears to be constant, as indicated by the precision of the measurements, the difference in Q (heat-of-reaction) across the transition region should be accurate within the experimental error of the work .

A design for a second-generation calorimeter which incorporates the basic principles of the isothermal constant volume - "constant pressure" calorimeter is now available. This calorimeter would operate adiabatically, eliminating the need for heat-leak corrections and would provide more accurate heat-of-reaction values.

CONCLUSIONS

The constant volume-"constant pressure" combustion calorimeter is a useful tool for investigating pressure-activated reaction transitions. It has shown that 4.1μ to 92μ β-HMX experiences a reaction transition that is independent of particle size as it burns between 20,700 and 34,500 kPa (3000 and 5000 psi) during which its heat-of-reaction (Q) increases 4.27 ± 0.26 x 10^5 J/kg (102 ± 6 cal/g).

This transition occurs in the pressure region of the burning rate discontinuity observed for propellants containing this explosive. Its presence provides insight into this particular problem area and opens up interesting avenues of investigation.

RECOMMENDATIONS

It is recommended that work be continued in this area to determine the nature of this reaction transition. It is also recommended that the adiabatic version of the constant volume - "constant pressure" calorimeter be constructed and that the investigation be extended to related nitramine explosives.

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